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<b>(21) International Application Number:</b> PCT/NO92/00193 <b>(22) International Filing Date:</b> 9 December 1992 (09.12.92) <b>(30) Priority data:</b> 915080 23 December 1991 (23.12.91) NO <b>(71) Applicant (for all designated States except US):</b> NORSK HYDRO A.S [NO/NO]; N-0240 Oslo (NO). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> KVISLE, Steinar [NO/NO]; Breidablikkbakken 44, N-3900 Porsgrunn (NO). WENDELBO, Rune [NO/NO]; Per Gynts vei 2, N-0851 Oslo (NO). ØREN, Hanne [NO/NO]; Grensefaret 25, N-1362 Billingstad (NO). <b>(74) Agent:</b> ANDERSON, Elin; Norsk Hydro a.s, N-0240 Oslo (NO).		<b>(81) Designated States:</b> AT, AU, BB, BG, BR, CA, CH, CS, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCEDURE FOR SYNTHESIS OF CRYSTALLINE MICROPOROUS SILICO-ALUMINO-PHOSPHATES  <b>(57) Abstract</b>  The application concerns an improved method of producing silico-alumino-phosphate catalysts for the conversion of methanol into light olefins such as ethylene and propylene (the MTO reaction). The improved method of synthesis can be used to control chemical composition of the silico-alumino-phosphates, especially the silicon content. In particular, it was found that catalysts can be synthesized that are more stable to deactivation by "coking", which is very important for the design of an MTO process based on the synthesized silico-alumino-phosphates.		

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"Procedure for synthesis of crystalline microporous  
silico-alumino-phosphates"

The application concerns a procedure for the production of crystalline microporous silico-alumino-phosphates with a controlled silicon content, a crystalline microporous silico--alumino-phosphate with improved stability to deactivation and an application of this in the production of olefins from methanol.

We are familiar from Norwegian Patent Application No. 832712 with microporous crystalline silico-alumino-phosphates and a procedure for synthesizing such products. These products have a three-dimensional space lattice built up from  $\text{PO}_2^+$ ,  $\text{AlO}_2^-$  and  $\text{SiO}_2$  tetrahedral units, whose most important chemical composition on a water-free basis is:



where "R" represents at least one organic template material which is present in the intracrystalline pore system; "m" is the number of moles of "R" present per mole of  $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$  and m has a value between 0 and 0.3, the maximum value in each case being dependent on the molecular dimensions of the template material and the available pore volume in the silico-alumino-phosphate structure in question; "x", "y" and "z" are molar fractions of silicon, aluminium and phosphorus respectively, present as tetrahedral oxides. The minimum value of "x", "y" and "z" is 0.01, and the maximum value of "x" is 0.98, of "y" 0.6 and of "z" 0.52. The minimum value of "m" in the formula above is 0.02.

The reaction mixture is achieved by combining at least one part each of the aluminium and phosphorus sources in the absence of the silicon source. Then the resultant mixture is reacted with

the remaining components to get the total reaction mixture.

The reaction mixture is placed in a pressure vessel for shaking then heating under autogenic pressure to a temperature of at least 100 °C, and preferably between 100 and 260 °C, until a crystalline silico-alumino-phosphate is obtained. The product is extracted in any appropriate way, for example by centrifuging or filtering.

It is generally known that the chemical composition of the silico-alumino-phosphates is very important for their physical and chemical properties, including their properties when used as catalytic materials. It would therefore be a great advantage if one could use production methods for silico-alumino-phosphates where the chemical composition of the product can be variably controlled. This is particularly true of the silicon content. The known technique makes no allowance for this. In syntheses of SAPO-34 in NO 832712, for example, there is a poor match between the chemical composition of the synthesis gel and the synthesized silico-alumino-phosphate.

According to the examples in NO 832712, equimolar quantities of aluminium oxide and phosphorus pentoxide are used to synthesize SAPO-34. Since Si partly replaces P in the SAPO structure, a mixture is obtained where an excess of P has arisen in the form of phosphoric acid. The amount of Si which replaces P, and thus the composition of the end product, does not seem to be controllable in these syntheses.

After a period of time, all catalysts used to convert methanol to olefin (the MTO reaction) lose their active ability to convert methanol to hydrocarbons - that is, the catalyst is deactivated. With MTO catalysts of the molecular sieve type, this is because the microporous crystal structure is filled up with low-volatility carboniferous compounds which block the pore structure. This is often called deactivation by "coking". The carboniferous compounds can be removed by combustion in

air. This is a familiar technique.

Deactivation can also take the form of the collapse of the space lattice, but this kind of deactivation takes place over a much longer timescale than deactivation by coking.

Stability to deactivation by coking is a very important property for an MTO catalyst, so it would be a great advantage if one could produce MTO catalysts with improved stability to deactivation by coking.

The object of the invention is thus to produce crystalline microporous silico-alumino-phosphates with controlled silicon content. Another object is to produce silico-alumino-phosphates which have an enhanced stability to deactivation by coking.

These and other objects of the invention are achieved by means of the procedure described below, and the invention is characterized and defined by the patent claims listed at the end of this application.

With this invention we have arrived at a method by which the chemical composition of the product can be controlled. Surprisingly, we have found that this can be done by mixing the aluminium, silicon and phosphorus sources in the synthesis gel in the same proportions as required in the finished silico-alumino-phosphate. To achieve this it is necessary to have a small excess of phosphoric acid corresponding to the amount remaining in the fluid phase after complete crystallization. Furthermore, another acid than phosphoric acid must be added. We have preferred to use hydrochloric acid. The composition of the end product can be accurately controlled, and as a result, silico-alumino-phosphates can be synthesized with the desired silicon content. This can in general be used to optimize the chemical properties of silico-alumino-phosphates used as catalysts.

To synthesize silico-alumino-phosphates according to the invention, the aluminium source is mixed with the phosphorus source and the acid additive. The mixture is homogenized before the silica source is added. The gel formed is homogenized before adding the template material. After homogenization, the mixture is poured into a pressure vessel and shaken at room temperature, then heated. The solid reaction product is recovered and dried.

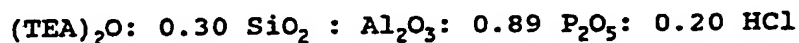
The sequence of the process stages is not critical, but the extra acid additive (preferably HCl) must be added along with the phosphorus source. It was found that the molar ratio of silica to HCl must be kept between 0.3 and 3. The preferred ratio is 1-2.

In synthesizing silico-alumino-phosphates, the choice of sources for aluminium oxide, silica and phosphorus pentoxide is not critical. For example, aluminium propoxide, phosphoric acid and silica sol can be used. As template materials, tetraethyl ammonium hydroxide solution, cyclopentylamine, aminomethyl cyclohexane, piperidine, cyclohexylamine and triethyl hydroxyethylamine can be mentioned as suitable materials.

The invention will be further illustrated by the following examples. In the examples the improved method of synthesis is used to produce the material SAPO-34 in particular, but can be generally used to synthesize all types of silico-alumino-phosphates.

Example 1

To synthesize SAPO-34, a reaction mixture was made by combining 27.2 g of aluminium isopropoxide with a mixture of 13.7 g of 85% phosphoric acid and 1.4 g of 37% hydrochloric acid in 36.3 g of distilled water. The mixture was homogenized by agitation for one minute in a 250 ml PE bottle. To this mixture was added 4.0 g of a 30% silica sol in water, and the gel which formed was homogenized in the same way as described above. The mixture was left to stand for five minutes. Then 49.2 g 40% of an aqueous solution of tetraethyl ammonium hydroxide was added, and this mixture was homogenized as described above. The composition of the finished reaction mixture in mole ratios was:

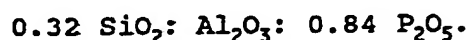


The mixture was then poured into a stainless steel pressure vessel lined with an inert material, and this was placed in a heat block. The heat block and pressure vessel were agitated on a vibration table for 16 hours at room temperature. The mixture was then heated to 215°C, and was kept at this temperature for 99 hours. The solid reaction product was recovered by centrifuging, washed in 150 ml of distilled water and then centrifuged again. It was then dried in air at 110°C overnight. The product was crystalline, and consisted of SAPO-34 with an X-ray powder diffraction pattern (XRD) characterized by the following data:

TABLE 1.

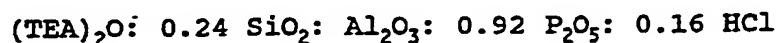
2 $\theta$	d	100xI/I <sub>0</sub>
9.49	9.32	100
12.80	6.92	15
14.07	6.29	16
15.98	5.55	49
20.54	4.33	74
22.27	3.991	5
23.06	3.857	5
25.26	3.526	19
25.80	3.453	15
27.57	3.236	4
28.42	3.140	3
29.52	3.026	5
30.51	2.930	25
31.28	2.866	17

The product was calcinated in dry air at 600°C for two hours, and then analysed. Chemical analysis determined that the composition of the solid, calcinated product was 42.4 weight % Al<sub>2</sub>O<sub>3</sub>, 8.1 weight % SiO<sub>2</sub>, 49.5 weight % P<sub>2</sub>O<sub>5</sub>, which gave a product composition in terms of the main components of:



#### Example 2

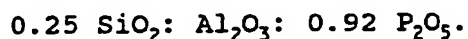
SAPO-34 was synthesized with the same prescription as described in Example 1, but the amount of silica sol added was less (3.2 g); less hydrochloric acid was added (1.1 g); but more phosphoric acid (14.2 g), such that the composition of the finished reaction mixture in mole ratios was:



The product was recovered as described in Example 1 and was characterized by an XRD pattern without significant deviations

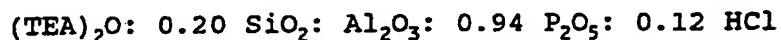


from the one shown in Table 1. Chemical analysis of the calcinated product revealed a product composition in terms of main components of:

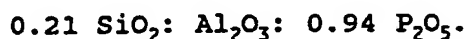


### Example 3

SAPO-34 was synthesized with the same prescription as described in Example 1, but the quantity of silica sol added was less (2.6 g); less hydrochloric acid was added (0.9 g), but more phosphoric acid (14.5 g) such that the composition of the finished reaction mixture in mole ratios was:

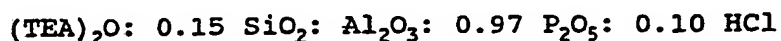


The product was recovered as described in Example 1 and characterized by an XRD pattern in all essentials as in Table 1. Chemical analysis of the calcinated product revealed a product composition in terms of main components of:



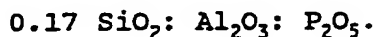
### Example 4

SAPO-34 was synthesized with the same prescription as described in Example 1, but the quantity of silica sol added was less (2.0 g); less hydrochloric acid was added (0.7 g); but more phosphoric acid (14.9 g), such that the composition of the finished reaction mixture in mole ratios was:



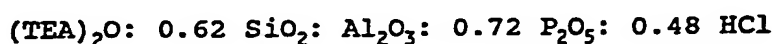
The product was recovered as described in Example 1 and characterized by an XRD pattern in all essentials as in Table 1.

Chemical analysis of the calcinated product revealed a product composition in terms of main components of:

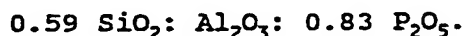


#### Example 5

SAPO-34 was synthesized with the same prescription as described in Example 1, but the quantity of silica sol added was greater (8.2 g); more hydrochloric acid was added (3.2 g); but less phosphoric acid (11.0 g) such that the composition of the finished reaction mixture in mole ratios was:

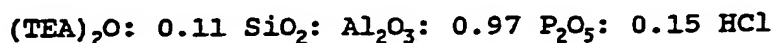


The product was recovered as described in Example 1 and characterized by an XRD pattern in all essentials as in Table 1. Chemical analysis of the calcinated product revealed a product composition in terms of main components of:



#### Example 6

SAPO-34 was synthesized with the same prescription as described in Example 1, but the quantity of silica sol added was less (1.5 g); less hydrochloric acid was added (1.1 g); but more phosphoric acid (15.0 g), such that the composition of the finished reaction mixture in mole ratios was:



The product was recovered as described in Example 1 and characterized by an XRD pattern in all essentials as in Table 1.

Table 2 sums up the molar composition of the synthesis gel and the synthesized silico-alumino-phosphates in Examples 1-6.

**TABLE 2.** Molar composition of synthesis mixture and products in Examples 1-6.

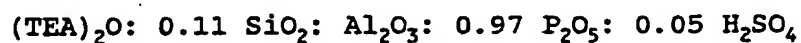
Example #	SYNTHESIS GEL			SYNTHESIS PRODUCT		
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
1	0.30	1.00	0.89	0.32	1.00	0.84
2	0.24	1.00	0.92	0.25	1.00	0.92
3	0.20	1.00	0.94	0.21	1.00	0.94
4	0.15	1.00	0.97	0.17	1.00	1.00
5	0.60	1.00	0.75	0.59	1.00	0.83
6	0.11	1.00	0.97	0.09	1.00	0.96

The results in Table 2 illustrate how the enhanced method of synthesis can be used to control the variation of the silicon content in SAPO-34.

The synthesis examples are described with the addition of hydrochloric acid to regulate the PH of the gel. Tests were done to establish whether the addition of other acids produced the intended effect. Examples 7 and 8 describe the use of sulphuric and nitric acid respectively instead of hydrochloric acid.

#### Example 7

SAPO-34 was synthesized with the same prescription as described in Example 6, but instead of 1.1 g of 37% hydrochloric acid, 0.7 g of concentrated sulphuric acid was added, such that the composition of the finished reaction mixture in mole ratios was:



The product was recovered as described in Example 1 and characterized by an XRD pattern with the following data:

TABLE 3.

2 $\theta$	d	100xI/I <sub>0</sub>
7.44	11.9	100
9.49	9.31	29
12.90	6.86	12
14.08	6.29	5
14.96	5.92	21
15.98	5.54	13
19.83	4.47	40
20.53	4.32	25
21.08	4.21	42
21.50	4.13	10
22.48	3.955	55
23.10	3.850	4
24.85	3.583	5
25.30	3.521	8
26.06	3.419	16
27.68	3.222	2
28.32	3.151	4
29.15	3.063	10
30.18	2.962	13
30.50	2.930	9
31.32	2.856	7
33.79	2.653	4

The X-ray data in Table 3 shows that the product mainly consists of SAPO-5 with some SAPO-34.

Example 8

SAPO-34 was synthesized with the same prescription as described in Example 6, but instead of 1.1 g of 37% hydrochloric acid, 1.0 g of 65% nitric acid was added, such that the composition of the finished reaction mixture in mole ratios was:

(TEA)<sub>2</sub>O: 0.11 SiO<sub>2</sub>: Al<sub>2</sub>O<sub>3</sub>: 0.97 P<sub>2</sub>O<sub>5</sub>: 0.07 HNO<sub>3</sub>

The product was recovered as described in Example 1 and characterized by an XRD pattern with the following data:

TABLE 4.

2θ	d	100xI/I <sub>o</sub>
7.45	11.9	36
9.51	9.29	100
10.80	8.19	5
12.82	6.90	11
14.07	6.29	12
14.92	5.94	10
15.53	5.70	15
15.97	5.55	29
16.97	5.22	25
19.87	4.47	15
20.53	4.32	42
20.99	4.23	28
22.46	3.959	16
24.38	3.650	5
25.33	3.516	14
25.81	3.452	12
26.14	3.409	11
26.79	3.328	6
29.13	3.065	5
30.16	2.963	11
30.51	2.930	16
31.32	2.856	17

The XRD data in Table 4 show that the product mainly consists of SAPO-34, but with a considerable percentage of SAPO-5.

The characterization of the products in Examples 7 and 8 by their powder X-ray diffractogram shows that impurities were obtained. This indicates that hydrochloric acid is the preferred reagent for synthesizing a product with controlled composition.

It was found that the present invention provides optimum introduction and distribution of silicon in the crystal lattice of the silico-alumino-phosphates, and improved morphological properties. This was demonstrated by comparing silico-alumino-phosphates with the same silicon content, synthesized respectively with the present invention and with the known technique.

The examples show the catalytic application for the synthesis of light olefins from methanol as raw material. In general the improved silico-alumino-phosphates can be used for catalytic conversion of a raw material which includes aliphatic hetero-compounds like alcohols, ethers, carbonylic compounds like aldehydes and ketones, halogenides, mercaptans, sulphides and amines to a hydrocarbon product containing light olefins like ethylene, propylene and butenes. The aliphatic hetero-compound may be pure, in a mixture with others of the specified aliphatic hetero-compounds, or mixed with a diluent such as water, nitrogen, a hydrocarbon etc.

The raw material is brought into contact with the molecular sieve synthesized as in the invention in conditions which lead to efficient conversion into light olefins. Use of a diluent, especially water, is preferable in this reaction.

The process can be carried out in all the familiar reactor types, including fixed bed and fluidized reactors. The catalyst is prepared as necessary for use in the various reactor types. The techniques for such preparation are familiar and will not be described in this application.

The materials synthesized in Examples 1-6 were tested as catalysts in the conversion of methanol into light olefins (Exx. 9-14). All the materials were calcinated at a high temperature before testing to remove traces of template material in the microporous structure.

These tests were done in a steel reactor with an outside diameter of  $\frac{1}{2}$ ". 0.5 g of catalyst, screened to 35-70 US standard mesh, was used. Quartz particles were laid over and under the catalyst particles. The reactor was heated by an outside electric heater and the reactor temperature was measured with a thermo element. The reactor temperature in all examples described below was 425 °C. Methanol was fed with a precision pump (ISCO LC 5000) and diluted with nitrogen gas, such that the partial pressure of methanol was 0.4 bars. Total pressure in the reactor was about 1.2 bars. The product gas from the reactor was conducted through a condenser cooled by ice water before the product composition was determined by gas chromatography.

The methanol conversion was 100% in the tests, with a carbon balance close to 100%. As a measure of the stability of the catalyst to deactivation, the interval before breakthrough of dimethyl ether was used. With the breakthrough of DME the conversion of oxygenates to light olefins is less than 100%, and the catalyst must be regenerated.

Table 5 shows the interval before breakthrough for the catalysts synthesized in Examples 1-6 above.

TABLE 5.

Time before breakthrough of DME in MTO reaction for materials synthesized in Examples 1-6.

Example #	Silicon content <sup>1</sup>	Breakthrough of DME (mins.)
9	0.32	375
10	0.25	435
11	0.21	375
12	0.17	375
13	0.59	325
14	0.09	415

1. Relative to  $\text{Al}_2\text{O}_3$  (1.0).

The results in Table 5 indicate that the Si content is important for stability to deactivation by coking. The sample with the lowest Si content exhibited the greatest stability, while the sample with the highest Si content was poorest in this respect. Table 6 shows the product distribution in Example 10. Product distribution in the other examples is quite comparable.

TABLE 6. Product distribution (carbon selectivities at breakthrough of DME) in catalytic test of catalyst synthesized in Example 10.

Methane	Ethene	Ethane	Propene	Propane	Butanes	Butenes	C5+	CO	CO <sub>2</sub>
1.6	43.9	1.0	42.0	0	0.1	9.8	1.1	0.2	0.3

#### Example for comparison

In order to compare this with the familiar technique, SAPO-34 was synthesized as in NO 832712 (Exx. 15-19). This method does not involve the use of HCl to control the silicon content of the synthesized SAPO-34. Five materials were synthesized with respective silicon contents of 0.14, 0.19, 0.23, 0.29 and 0.56, in other words samples with silicon contents comparable to



those in Examples 1-5.

TABLE 7. Time before breakthrough of DME in MTO reaction for materials synthesized as in NO 832712.

Example #	Silicon content <sup>1</sup>	Breakthrough of DME (mins.)
15	0.14	295
16	0.19	325
17	0.23	325
18	0.29	325
19	0.56	325

1. Relative to Al<sub>2</sub>O<sub>3</sub>

With the exception of the sample with a relative molar Si content of 0.14, the table shows that all the samples exhibited the same interval before breakthrough of DME. This interval was 325 mins. The sample with the lowest Si content took 295 mins. Comparing with Table 5, one sees that samples with comparable Si content, synthesized as in the present invention, exhibit better stability to deactivation than samples with the same Si content, synthesized by the familiar technique. This is evident from the fact that all the samples synthesized by the familiar technique exhibit a shorter interval before breakthrough of DME than samples synthesized in accordance with the present invention. This may be because the method described here provides a more favourable introduction of Si into the space lattice of the silico-alumino-phosphates and a better morphology, without this possible explanation implying any limitations on the invention.

Patent claims

1. Procedure for producing crystalline microporous silico-alumino-phosphates with controlled Si content from a mixture of reactive sources of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  and an organic template material, where the mixture is produced by combining at least a portion of the Al source and the P source in the absence of the Si source and then mixing the resulting mixture with the other ingredients, characterized in that the aluminium and silicon sources in the synthesis gel are mixed in the same mole ratios as in the desired product composition, the phosphorus source is added in excess and an acid is added.
2. Procedure according to Claim 1, characterized in that the excess of the phosphorus source is added corresponding to the amount remaining in the fluid phase after complete crystallization.
3. Procedure according to Claim 1, characterized in that the acid additive used is hydrochloric acid.
4. Procedure according to Claim 1, characterized in that the acid is added in a quantity such that the ratio of silica to hydrochloric acid in the gel is kept between 0.3 and 3, preferably between 1 and 2.
5. Procedure according to Claim 1, characterized in that tetraethyl ammonium hydroxide, cyclopentylamine, aminomethyl-cyclohexane, piperidine, cyclohexylamine and triethyl-hydroxyethylamine are used as template material.

6. Crystalline microporous silico-alumino-phosphates with improved stability to deactivation by coking, characterized in that they are synthesized from a mixture of reactive sources of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  and an organic template material, where the aluminium and silicon sources in the synthesis gel are present in the same mole ratio as in the desired product composition, the phosphorus source is present in excess and with an extra acid additive.
7. Silico-alumino-phosphates according to Claim 6, characterized in that the excess of the phosphorus source is present in a quantity corresponding to the amount remaining in the fluid phase after complete crystallization.
8. Silico-alumino-phosphates according to Claim 6, characterized in that hydrochloric acid is present as an extra acid additive in a quantity such that the ratio of silica to hydrochloric acid in the gel is 0.3-3, with a special preference for 1-2.
9. Silico-alumino-phosphates according to Claim 6, characterized in that they at least exhibit an X-ray powder diffraction pattern characterized by data as given in Table 1.
10. Use of crystalline microporous silico-alumino-phosphates synthesized from a mixture of reactive sources of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  and an organic template material, where the aluminium and silicon sources in the synthesis gel are present in the same mole fractions as in the desired product composition, the phosphorus source is present in excess and with an extra acid additive, as a catalyst in the synthesis of olefins from methanol.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 92/00193

## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C01B 25/45

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C01B, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US, A, 5096684 (FRANCOISE GUTH ET AL), 17 March 1992 (17.03.92), column 2, line 24 - line 38	1-10
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A	US, A, 4440871 (BRENT M. LOK ET AL), 3 April 1984 (03.04.84)	1-10
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☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

15 March 1993

Date of mailing of the international search report

23 -03- 1993

Name and mailing address of the ISA/  
 Swedish Patent Office  
 Box 5055, S-102 42 STOCKHOLM  
 Facsimile No. +46 8 666 02 86

Authorized officer

May Hallne  
 Telephone No. +46 8 782 25 00

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

29/01/93

International application No.  
PCT/NO 92/00193

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US-A-	5096684	17/03/92	EP-A-	0391774	10/10/90
US-A-	4440871	03/04/84	CA-A-	1202016	18/03/86
			EP-A,B-	0103117	21/03/84
			SE-T3-	0103117	

